Side-Chain Crystallinity. I. Heats of Fusion and Melting Transitions on Selected Homopolymers Having Long Side Chains

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Synopsis

Heats of fusion, melting transitions, and the derived entropies of fusion were obtained by differential scanning calorimetry for examples from three homologous series of homopolymers having long side chains. Homopolymers having side-chain lengths between 12 and 22 carbon atoms were chosen from the poly(*n*-alkyl acrylates), the poly(*N*-*n*-alkylacrylamides) and the poly(vinyl esters). The data demonstrated that only the outer paraffinic methylene groups were present in the crystal lattice. This was concluded because phase diagrams obtained for mixtures of structurally different monomers and homopolymers, as well as for selected copolymers, showed only isomorphism in the polymeric examples. In addition, scanning curves, reflecting the distribution of crystallite sizes, became narrower as the side chains became longer. The critical chain length required to maintain a stable nucleus in the bulk homopolymers was a constant value for each homologous series. It varied between 9 to 12 carbon atoms. When heats of fusion were determined in the presence of methanol, main-chain restraints were freed, thus permitting more methylene groups to enter the crystal lattice. Hence, the heats of fusion, the crystallinity, and melting points increased above that of the bulk state. The magnitude of the contribution to the heats of fusion by each methylene group indicated that the hexagonal paraffin crystal modification prevailed in these homopolymers, in agreement with x-ray data from the literature.

INTRODUCTION

Side-chain crystallinity is usually present in atactic vinyl homopolymers having linear subgroups in excess of 10–12 carbon atoms.[1] This was demonstrated by the first-order melting transitions obtained for largely atactic homologs selected from the poly(*n*-alkyl acrylates and methacrylates)[2,3] and their copolymers,[3] the poly-2-*n*-alkyl-1,3-butadienes,[4] the poly(vinyl esters),[5] the poly-*n*-alkylstyrenes,[6] the poly-*N*-*n*-alkylacrylamides,[7] and the poly(fluoro-*n*-alkyl acrylates).[8] Crystallinity was also shown to be present only in the side chains of the isotactic poly(*n*-alkyl acrylates),[9] by using x-ray diffraction, although the degree of tacticity was not specified in the citation. In highly crystalline isotactic poly-1-alkenes, however, x-ray diffraction demonstrated that both main and side chains were in the crystal.[10]

On rapid quenching of polyoctadecene-1 from the melt and extracting, a fraction melting at 41°C was obtained[11] which was thought to involve only crystallinity in the side chains. This conclusion was reached because most atactic 17- and 18-carbon homopolymers melt at about 45–55°C.

The utilization of vinyl monomers derived from animal fats suffers to some extent because of the rigidity introduced into homopolymers and copolymers by side-chain crystallinity. When they are used as internal plasticizers, brittle failure usually results at high plasticizer content.[7,12] Consequently, a more systematic and quantitative thermodynamic study of the crystallinity phenomenon seemed to be warranted. This paper reports the results of using differential scanning calorimetry to obtain the heats of fusion, melting transitions and derived entropies of fusion for three representative homologous series of homopolymers, namely the poly(*n*-alkyl acrylates) the poly-*N*-*n*-alkylacrylamides, and the poly(vinyl esters). Evidence will be presented indicating that the side chain crystal lattice is entirely paraffinic, with no incorporation of main-chain units. Phase diagrams, constructed for mixtures of homopolymers and for copolymers, will be introduced in support of this view. Estimates of crystallinities will be obtained from the thermodynamic quantities obtained. In subsequent papers the influence of side chain crystallinity on the glass transition[13] and the mechanical properties[14] of copolymers will be treated.

EXPERIMENTAL

Amines and Alcohols

The amines and alcohols, the purest available commercially (specified to be greater than 99% pure by gas-liquid chromatography), were used directly.

Monomer Preparation and Purification

The preparation and purification of *N*-*n*-octadecyl-[12] and *N*-*n*-dodecylacrylamide[7] have been described. The remaining *N*-*n*-alkylacrylamides were prepared[12] and the tetradecyl-,[7] *N*-*n*-hexadecyl-[12] and *N*-*n*-docosylacrylamides[12] purified by the designated literature procedures. Yields, melting points (fused sample), acid number, and purity by gel-permeation chromatography, respectively, were: C_{14}, 82.8%, 63.5–64.0°C, 0.19, 99.9%; C_{16}, 76.4%, 70.0–70.5°C, 99.9%; C_{22}, 67.6%; 80.5–82.0°C, 0.47, 85.8%.

ANAL. C_{14}, Calcd: C, 76.34%; H, 12.44%; N, 5.24%. Found: C_{14}, C, 76.26%; H, 11.99%; N, 5.50%. C_{16}, Calcd: C, 77.23%; H, 12.62%; N, 5.41%. Found: C, 76.71%; H, 12.29%; N, 4.69%. C_{22}, Calcd: C, 79.08%; H, 12.74%; N, 3.69%. Found: C, 78.53%; H, 12.93%; N, 3.61%.

The *n*-alkyl acrylates were prepared by the same procedure used for the *N*-*n*-alkylacrylamides.[12] Each crude ester was taken up in a low-boiling (63–70°C) commercial alkane mixture (3 ml/g) and treated twice with equal volumes of 10% sodium carbonate to remove acid. The isolated C_{12}

and C_{14} were flash-distilled at 0.1 mm Hg and crystallized twice from acetone (3 ml/g), the C_{12} at $-60°C$ and the C_{14} at $-20°C$. The balance of the esters were crystallized from the alkane mixture at $-20°C$ and recrystallized from acetone (3 ml/g), at 0°C, except for the hexadecyl ester which was recrystallized at $-20°C$. Yields were: C_{12}, 77.7%; C_{14}, 62.9%; C_{16}, 61.2%; C_{18}, 53.0%, C_{22}, 45.6%. Purity by gel-permeation chromatography was: C_{12}, 98.3%; C_{14}, 84.6%; C_{16}, 99.7%; C_{18}, 99.5%; C_{22}, 92.7%.

ANAL. C_{12}, Calcd: C, 74.95%; H, 11.74%. Found: C, 75.24%; H, 11.77%. C_{14}, Calcd: C, 76.06%; H. 12.02%. Found: C, 76.22%; H, 11.99%, C_{16}, Calcd: C, 76.98%; H, 12.24%. Found: C, 77.09%; H, 12.02%; C_{18}, Calcd: C, 77.72%; H, 12.42%. Found: C, 77.96%; H, 12.47%. C_{22}, Calcd: C, 78.88%; 12.71%. Found: C, 78.97%; H, 12.77%.

Vinyl laurate and palmitate were prepared[15] and vinyl laurate was purified by a reported procedure.[15] Vinyl palmitate was chromatographed on dry Fluorosil and eluted with hexane. Both esters were 99% pure by gas-liquid chromatography. Vinyl stearate, obtained from commercial sources, was crystallized from acetone (10 ml/g) four times at $-20°C$ and was 98.8% pure by gas-liquid chromatography.

Polymerization Procedure

The monomers were polymerized in benzene (3 mole/mole of monomer) at 60°C for 48 hr in sealed bottles under nitrogen with the use of 0.1 mole-% of azobisisobutyronitrile as initiator. Exceptions were *n*-docosyl acrylate (19 hr) and *N*-*n*-docosylacrylamide (19 hr at 90°C). The homopolymers were precipitated in methanol and extracted free of monomer using this solvent at reflux. All of the homopolymers were freed of solvent by drying under vacuum from thin films. Within experimental error, the elemental analyses gave the expected values for carbon, nitrogen, etc., for each homopolymer.

Molecular Weight Measurements

The osmometric procedure was described;[12] gel-permeation chromatography was performed at the Analytical Service Laboratory of Waters Associates, Inc., Framingham, Mass.

The quantities A_n and A_w are defined as

$$A_n = (1/Q)\bar{M}_n$$
$$A_w = (1/Q)\bar{M}_w$$

where A_n is the number average molecular length and Q is a constant characteristic of the polymer. The ratio A_w/A_n was taken as a quantitative measure of dispersity.

Calorimetric Procedures

A Perkin-Elmer differential scanning calorimeter, DSC-1, was used. A set of standard operating conditions was adopted after a series of trials.

These were: scanning speed 10°C/min, attenuation selector setting 8 mcal/sec, and chart speed 1 in./min. Temperature readings were regulated for direct dial read-out by adjusting the average calibration to the correct melting temperature. For this a series of exceptionally pure fatty-acid derivatives was used as standards, having a spread of melting temperatures from −57 to 112°C. The parabolic calibration curve was then fitted by computer. Heats of fusion were checked using a sample of indium and the exceptionally pure naphthalene and benzoic acid used by Hampson and Rothbart.[16] A weighing procedure similar to that used by those authors was followed and values of the fusion heats close to theirs were obtained. These samples were checked periodically. Solid homopolymers were powdered and viscous samples were weighed into the sealable solvent cups provided with the instrument. Two different sample weights of each homopolymer were programmed, each through three successive heating and cooling cycles, from −73°C to 45°C above the melting transition. No low-temperature polymorphic transitions were observed with any of these homopolymers. Liquid nitrogen cooling was used for all determinations and calibrations. One determination in each set of three was carried out following rapid cooling by manual control, but no differences in melting peak areas were ever noticed by this quenching technique. Fusion endotherms always equaled crystallization exotherms within experimental error. A planimeter was used to measure peak areas; average values of the heats of fusion were reported. Average error in the heats of fusion was estimated to be about 1%. Samples run in methanol or *n*-decane were first melted and weighed as chunks into the solvent cups; the solvent was then introduced and the cups were sealed. No solvent or polymer loss occurred. Mixtures of homopolymers were fused in an oven at 140°C for one hour and then ground and weighed on cooling. The ends of the fusion curves were taken as the temperature of melting in all of the experiments, partly because this procedure gave the most regular value as side-chain length was varied. The last disappearance of crystallinity is the usual criterion for equilibrium melting.[17a] However, at the heating rates employed in this work, equilibrium could only have been approached. All computations were made by use of an IBM 1130 computer.

Refractometric Melting Temperature

Selected samples were run by a refractometric technique,[2] from 15°C below the transition, at an incremental heating rate of 1°C every 30 min. Usually no change occurred in refractive index after 5 min. Consequently, these transitions were considered to be equilibrium melting points.

RESULTS AND DISCUSSION

Thermodynamic Data and Molecular Weight and Size Measurements

The molecular weights, heats of fusion and melting transitions for the three homologous series are listed in Table I. Some melting points obtained at

low heating rates (ca. 1°/30 min) by refractometry are also included. They are usually lower than those by differential scanning calorimetry. They are probably more accurate because the fast scanning speeds (10°C/min) of the latter determination allowed insufficient time to reach equilibrium.[17a] Individual members of a homologous series of homopolymers are often designated in this paper by the number of side-chain methylene groups n.

The molecular weight data is typical of that obtained for the higher homologs.[18] The distribution curves from gel permeation chromatography showed a long tail at high elution volumes, indicating the presence of low molecular weight material in these unfractionated homopolymers. This accounts for the large value of the dispersity index. With the exception of the vinyl esters, the degrees of polymerization show that the samples were high polymers.

Heats of fusion and melting transitions were obtained in bulk for all of the homopolymers and some were determined in the presence of methanol, a non-solvent for the homopolymers. Methanol was used in highly varying amounts from sample to sample; the ratio of methanol to sample changed randomly from 0.16 to 1.4 down the list in Table I. Both types of data are listed in the table. Specific values of the bulk fusion endotherm were similar at each value of n for the poly(n-alkyl acrylates) and the poly(vinyl esters), allowing for the slight difference in n for these two systems, but are considerably lower for the respective poly-*N*-n-alkylacrylamides. However, in the presence of methanol the heats of fusion increased about 2 cal/g for the polyesters and 6 cal/g for the polyamides. In fact the heats of fusion for the poly-*N*-n-alkylacrylamides were similar after treatment to those for the bulk n-alkyl acrylates of the same side-chain length. Of greater significance, the melting transitions for most members of both ester and amide series were higher in methanol than in bulk. Phase-transition theory predicts a small decrease in temperature of melting as nonsolvent is increased,[17b] until the point where liquid–liquid phase separation exists, whereupon no further depression should occur. Consequently another explanation is required for an elevation of melting above that of the bulk state.

It is well known that certain liquids can, by solvation, increase the mobility of chains and thus greatly increase their rates of crystallization.[19–21] However, plasticization and bulk annealing should lead to the same thermodynamic transition[22] when equilibrium conditions prevail. In these systems methanol is thought to solvate the polar groups of the main chain and disrupt intramolecular interactions. This type of interaction is probably responsible for stiffness in these homopolymers[23] because intermolecular interactions are shielded by the side chains. Thus, as chain mobility is increased, more methylene groups in any chain unit can enter the crystal, thereby increasing the equilibrium crystallinity, the melting transitions, and the heats of fusion, as observed. This assumes, of course, that only side chains can crystallize.

Typical scanning curves are shown in Figure 1. These were drawn to equal weights and temperature increments. Insert 1 compares poly(n-

TABLE I
Molecular Weights, Heats of Fusion, and Melting Transition Temperatures for the Long Side-Chain Acrylates, Acrylamides, and Vinyl Esters

n[a]	Thermal analysis conditions	Conversion, %	Solution Properties			ΔH_f		T_m, °K	
			$\bar{M}_n$	DP_n	A_w/A_n	cal/g	cal/mole	DSC	Refractometer
			Poly-(*n*-alkyl acrylates)						
12	In bulk	86.8	223,700	930.6	9.12	8.75	2,103	285.0	
14		82.6	169,300	630.7	10.84	14.88	3,994	305.0	298.9
16		93.6	259,000	873.6	8.37	18.19	5,394	316.0	311.3
18		95.6	276,800	852.9	9.91	21.34	6,925	329.0	323.9
22		96.4	253,600	666.3		27.50	10,467	345.0	339.5
22		"	"	"		25.79	9,816	"	
16	In methanol		Same as above			20.37	6,041	321.0	
18						23.70	7,691	332.0	
22						27.85	10,601[b]	342.0	
			Poly-*N*-*n*-alkylacrylamides						
12	In bulk	77.8	448,900	1875.0	11.36	0.95	226	265.0	
14		96.8	505,200	1889.0	7.35	5.43	1,451	291.0	

16		96.6	551,100	1865.0	2.60	11.26	3,327	310.0	
16		"	"	"	"	7.70	2,274[c]	318.0	
18		98.2	244,350	755.2	7.65	12.96	4,193	321.0	
18		"	432,000	1335.0		11.96	3,870[c]	341.0	
22		90.4	199,900	526.5		21.15	8,029	341.0	
12	In methanol		Same as above			5.90	1,406	256.0	
14						12.90	3,450	299.0	306.7
16						16.97	5,015	315.0	317.4
18						20.33	6,578	330.0	327.8
22						23.24	8,823	346.0	
22	In 95% ethanol		Same as above			24.17	9,176	342.0	
			Poly(vinyl Esters)						
11	In bulk	65.3	51,700	228.4	2.23	5.78	1,308	289.0	301.5
15		68.0	59,600	211.0	1.98	17.37	5,150	319.0	316.1
17		82.0	48,900	157.5	2.46	19.82	6,154	331.0	327.6
15	In methanol		Same as above			18.84	5,586	318.0	
17						21.00	6,520	330.0	

[a] The number of side chain methylene groups.
[b] In 95% ethanol.
[c] Not used in the calculation of the parameters of Table III.

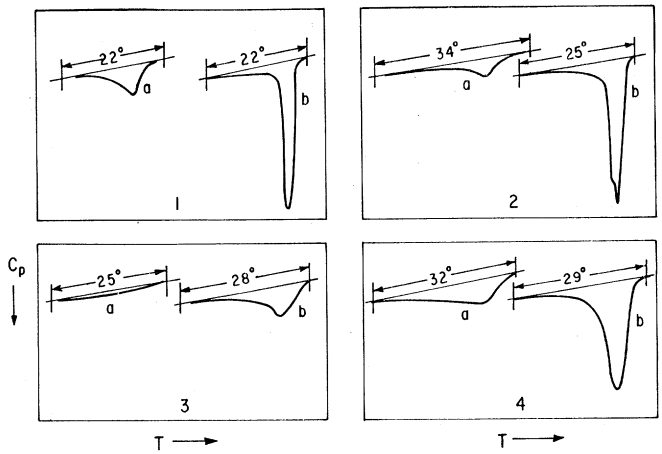

Fig. 1. Comparison of melting point curves for selected homopolymers: (*1a*) poly (*n*-dodecyl acrylate); (*1b*) poly(*n*-octadecyl acrylate); (*2a*) poly(vinyl laurate); (*2b*) poly(vinyl stearate); (*3*) poly*N*-*n*-dodecylacrylamide, (*a*) in bulk and (*b*) in methanol; (*4*) poly-*N*-*n*-octadecylacrylamide, (*a*) in bulk and (*b*) in methanol.

dodecyl acrylate) with poly(*n*-octadecyl acrylate); insert 2, poly(vinyl laurate) and poly(vinyl stearate); insert 3, poly-*N*-*n*-dodecylacrylamide, in bulk and in methanol, and insert 4, poly-*N*-*n*-octadecylacrylamide in bulk and in methanol. In all of the series, the overall melting range is similar, but there is a marked difference in the scanning curves. These curves qualitatively reflect the distribution of crystallite sizes.[22] In the ester homologs, the crystal-size spectrum becomes narrower and moves toward the higher temperature range of the distribution as the side chain length increases. This supports the view that only side chains crystallized in these systems. The amide crystal-size distributions are broader than those of the corresponding esters. The effect of added solvent in increasing both crystallinity and crystal perfection can be seen in inserts 3 and 4. At higher side chain length, poly-*N*-*n*-alkylacrylamides in methanol resembled the bulk esters of the same side chain length. The melting endotherms for the polyesters in methanol were slightly broader than for the corresponding bulk curves. Again, these data illustrate the effect of increased main-chain mobility on the development of crystallinity and the perfection of the crystals.

Entropies of fusion (listed in Table II) were determined from the usual relation

$$\Delta S_f = \Delta H_f / T_m \tag{1}$$

on the assumption that the melting transition T_m was the true equilibrium melting point, and that the heat of fusion represented that for the entirely crystalline phase.[17b] While melting points (Table I) by refractometry were believed to be equilibrium values, those by scanning calorimetry are not. Consequently, all of the entropies based on DSC measurements (Table II) will be somewhat more in error than those based on refractometry. Never-

TABLE II. Estimation of Crystallinity for the Long Side-Chain Acrylates, Acrylamides, and Vinyl Esters

n	Thermal analysis conditions	Crystallinity per unit x_c or x_c'		Crystalline CH_2 groups in side chain		Amorphous CH_2 groups in side-chain		ΔS_f, cal/mole-deg	
		Eq. (8)	Eq. (14)	Eq. (11)	Eq. (15)	Eq. (12)	Eq. (13)	Per unit	Per bond
				Poly(n-alkyl Acrylates)					
12	In bulk	0.17	0.16	2.9	2.8	9.1	9.2	7.38	2.64
14		0.28	0.25	5.4	4.8	8.6	"	13.36	2.78
16		0.35	0.32	7.3	6.8	8.7	"	17.33	2.55
18		0.41	0.38	9.4	8.8	8.6	"	21.39	2.43
22		0.52	0.47	14.2	12.8	7.8	"	32.76	2.56
22		0.49	"	13.4	"	8.6	"	31.23	2.44
16	In methanol	0.39	0.46	8.2	9.7	7.8	6.4	18.82	1.94
18		0.45	0.50	10.5	11.6	7.5	"	23.17	2.00
22		0.53	0.58	14.4	15.7	7.6	"	33.47	2.13
				Poly-N-n-alkylacrylamides					
12	In bulk	0.02	0.003	0.31	0.10	11.7	12.0	0.85	2.74
14		0.10	0.11	2.0	2.0	12.0	"	4.99	2.50
16		0.22	0.19	4.5	4.0	11.5	"	10.73	2.68
18		0.25	0.26	5.7	6.0	12.3	"	13.06	2.18
22		0.40	0.37	10.9	10.0	11.1	"	23.55	2.36
12	In methanol	0.11	0.15	1.9	2.5	10.1	9.5	5.49	2.20
14		0.25	0.24	4.7	4.5	9.3	"	11.25	2.50
16		0.32	0.31	6.8	6.5	9.2	"	15.80	2.43
18		0.39	0.37	8.9	8.5	9.1	"	20.07	2.36
22		0.44	0.46	12.0	12.5	10.0	"	25.50	2.04
22	In 95% ethanol	0.46	"	12.5	"	9.5	"	26.83	2.15
				Poly(vinyl Esters)					
11	In bulk	0.11	0.11	1.8	1.7	9.2	9.3	4.53	2.66
15		0.33	0.28	7.0	5.7	8.0	"	16.29	2.86
17		0.38	0.35	8.4	7.7	8.6	"	18.79	2.44
15	In methanol	0.36	a	7.6	a	7.4	a	17.57	2.31
17		0.40	a	8.9	a	8.1	a	19.76	2.22

[a] Insufficient data.

theless, a plot of ΔS_f against n for a composite of both types of data was linear, at least within the narrow range of n studied. Linearity is usually observed for correlations of enthalpy or entropy against chain length across short ranges of n.[24]

The relations[24] are

$$\Delta H_f(\text{cal/mole}) = \Delta H_{fe} + \alpha(n) \quad (2)$$

$$\Delta S_f(\text{cal/mole-deg}) = \Delta S_{fe} + \beta(n) \quad (3)$$

In eqs. (2) and (3), α and β represent the contribution of each added methylene group to the heat and entropy of fusion, respectively. Plots of ΔH_f against n in eq. (2) showed that n at $\Delta H_f = 0$ varied between 6.4 and 12.0 for the different systems. These values represent the sequence of methylene groups of a length insufficient to form a stable nucleus.[9] The quantities ΔH_{fe} and ΔS_{fe} are also constants reflecting contributions of the chain ends[24] to the respective enthalpic and entropic changes. The constants of eq. (2) and (3), obtained by curve-fitting the data by computer, are listed in Table III. The entropies of fusion are all very similar and are close to the value for polyethylene, 2.34 cal/mole-deg-CH_2.[17c] Similarly, all of the enthalpies, have like values, the average, 777 cal/mole-CH_2, being close to a value (735 cal/mole-CH_2) found for the α-hexagonal-to-liquid transition ($\alpha_H \rightarrow 1$) exhibited by alkanes close to their melting points.[25] The significance of both of these observations will be treated in the last section of this paper.

TABLE III
Parameters for Various Equations

Homopolymer	Thermal analysis conditions	Equation	Intercept, cal/mole	Slope, cal/mole-CH_2
n-Alkanes ($\alpha_H \rightarrow 1$)[a]		(8)	−2939.0 ± 422.8	734.9 ± 29.3
n-Alkyl acrylates	Bulk	(2)	−7271.0 ± 493.0	791.6 ± 27.8
" "	Methanol	(2)	−5989 ± 454.3	755.4 ± 24.1
N-*n*-Alkylacrylamides	Bulk	(2)	−9262.0 ± 788.6	774.8 ± 47.1
" "	Methanol	(2)	−6994.0 ± 681.3	734.7 ± 38.4
Vinyl esters	Bulk	(2)	−7686.0 ± 1651.0	829.5 ± 113.4
n-Alkyl acrylates	Bulk	(3)	− 21.24 ± 1.56[b]	2.41 ± 0.09[c]
" "	Methanol	(3)	− 20.78 ± 1.86[b]	2.46 ± 0.10[c]
N-*n*-Alkylacrylamides	Bulk	(3)	− 26.14 ± 2.00[b]	2.24 ± 0.12[c]
" "	Methanol	(3)	− 16.99 ± 2.39[b]	1.99 ± 0.13[c]
Vinyl esters	Bulk	(3)	− 22.02 ± 6.08[b]	2.46 ± 0.42[c]

[a] Data of Broadhurst.[25]
[b] In cal/mole-deg.
[c] In cal/mole-deg-CH_2.

Phase Diagrams for Mixtures of Homopolymers

If only the side chains can crystallize, phase diagrams for mixtures of any two homopolymers should form solid solutions. In contrast, mixtures of

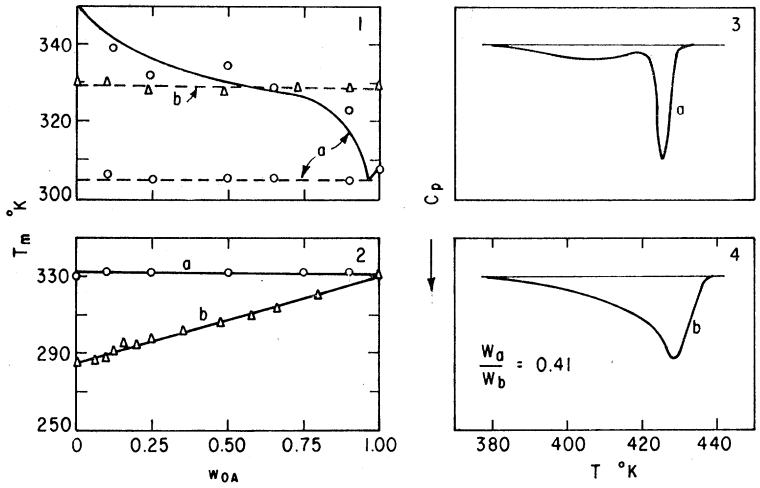

Fig. 2. Phase diagrams and DSC curves: (1) phase diagrams for (*a*) monomeric and (*b*) polymeric mixtures of *n*-octadecyl acrylate and *N*-*n*-octadecylacrylamide; (2) phase diagrams for copolymers of (*a*) *n*-octadecyl acrylate and vinyl stearate and (*b*) octadecyl acrylate and dodecyl acrylate; (*3*) DSC curves for mixtures, and (4) for copolymers, of *n*-octadecyl acrylate and *N*-*n*-octadecylacrylamide in bulk. w_{OA} is the weigh fraction of *n*-octadecyl acrylate. *W* is the sample weight.

their monomers should produce eutectic mixtures. Data are shown in Figure 2 for various homopolymer mixtures and copolymers. Insert *1a* shows a phase diagram for a mixture of monomeric *n*-octadecyl acrylate with *N*-*n*-octadecylacrylamide, while *1b* shows the respective homopolymer mixtures. Clearly the monomer mixtures show a eutectic; the homopolymers (curve *b*) only solid solutions, with no T_m depression. Insert 2 shows copolymers of (*a*) *n*-octadecyl acrylate and vinyl stearate and (*b*) copolymers of *n*-octadecyl acrylate and *n*-dodecyl acrylate. Isomorphism persists in both cases. In support of these observations solid solution formation between the higher methacrylate copolymers have long been known.[3] Differential scanning curves are shown in inserts 3 and 4 for (*a*) roughly a 50–50 mixture of poly-*n*-octadecyl acrylate) and poly-*N*-*n*-octadecylacrylamide and (*b*) their copolymers. The broad melting curve, characteristic of the amide homopolymers, persists in the mixtures, but is more diffuse in the copolymers, indicating a tendency toward more similar crystal sizes in the latter. Results like those of the figures were found by constructing phase diagrams for mixtures of poly(*n*-octadecyl acrylate) and poly(vinyl stearate) and by investigating 50–50 mixtures of all combinations of the other homopolymers with $n = 16$ and 22. A significant melting point depression was never found.

Heats of Fusion with a Diluent

The heat of fusion per mole of repeating unit is obtained using a diluent.[17b] When a sequence of methylene groups in the side chain constitutes the repeating unit, as in these homopolymers, the heat of fusion obtained with the

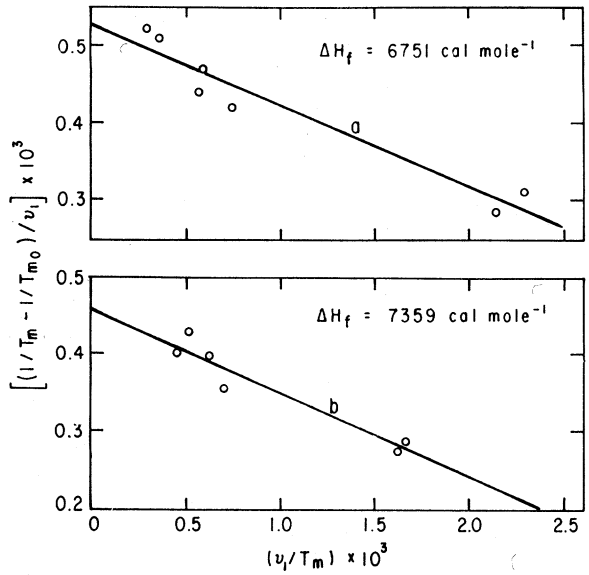

Fig. 3. Plot of the quantity $[(1/T_m) - (1/T_{m0})]/v_1$ against v_1/T_m for (*a*) poly-(*n*-octadecyl acrylate) and (*b*) poly(vinyl stearate) in the diluent *n*-decane.

use of a diluent will be a measure of its crystallinity. The ratio of the calorimetric heat to this quantity will decrease from unity to the extent that chain imperfections introduce sequences of amorphous units. The ratio will therefore represent the overall crystallinity of the sample. Consequently it will give some idea of the reliability of the calorimetric heats as a quantitative measure of the crystallinity present in each unit of the polymer chain.

The diluent method was used to measure the heat of fusion per repeating unit for poly(*n*-octadecyl acrylate) and poly(vinyl stearate). *n*-Decane was the diluent, and the melting point depression was determined by differential scanning calorimetry. The melting point depression was described by the relation

$$[(1/T_m) - (1/T_{m0})]/v_1 = (R/\Delta H_f)(V_u/V_1)[1 - (BV_1/R)(v_1/T_m)] \quad (4)$$

where T_m and T_{m0} are the equilibrium melting points for the homopolymer in the presence of diluent and in bulk, respectively, v_1 is the volume fraction of diluent, V_u/V_1 is the ratio of molar volumes of homopolymer and diluent, respectively, and ΔH_f is the heat of fusion. Densities for the homopolymers were estimated by use of group additivity correlations[26] for crystalline homopolymers; the value for poly(vinyl stearate) was checked by a solvent gradient method. The quantity B is related to the solvent–polymer interaction parameter, χ_1, by the equation

$$\chi_1 = BV_1/RT \quad (5)$$

The data are shown in Figure 3; ΔH_f is given in the figure. The value of ΔH_f for poly(*n*-octadecyl acrylate) was similar to that obtained by calorimetry (Table I); the value for poly(vinyl stearate) was somewhat higher by the diluent method. Consequently over-all crystallinity was nearly unity for poly(*n*-octadecyl acrylate) and 0.83 for poly(vinyl stearate). The high chain-transfer coefficient estimated for poly(vinyl stearate)[27] and its low molecular weight (Table I) suggest that branching caused the decrease in crystallinity. On the other hand, the approximations involving density leave the diluent heats somewhat in doubt. It is considered, however, in view of these experiments, as well as by the observation of the regularity of ΔH_f as n changes (Tables I and II), that most mers are involved in crystal domains. The x-ray data also indicated high levels of crystallinity in poly(vinyl stearate).[28] It remains to establish the extent of crystallinity present in each polymerizing unit.

Some other quantities of interest were obtained from the data using diluents. Heats of fusion were obtained by calorimetry for each point in Figure 3; they agreed with the value in the figure for the indicated homopolymer. Thus evidence is provided that the diluent, as required by theory,[29] was absent from the crystal lattice. In fact, *n*-decane was a thermodynamically rather poor solvent for the homopolymers. The value of B in eq. (4) was positive,[29] being 2.02 for poly-*n*-octadecyl acrylate) and 2.43 2.43 for poly(vinyl stearate).

Estimates of Crystallinity Present in the Side Groups

Crystallinity x_c in polymers can be estimated by calorimetry when the relation

$$x_c = \Delta H_f / \Delta H_{f0} \tag{6}$$

is satisfied.[30] ΔH_f is the observed calorimetric heat of fusion for the unit and ΔH_{f0} is the heat of fusion for the 100% crystalline phase. In these systems the crystalline phase was shown to constitute some fraction of the side chains. The x-ray diffraction has demonstrated[9,31] that the side chains of poly(vinyl stearate), as well as the side chains of the higher polymeric *n*-alkyl acrylates[9] and presumably the methacrylates, are arranged perpendicular to the plane of their chain ends in the rather loose hexagonal modification, assumed by many *n*-paraffins[25] a few degrees below their melting point. However, in poly(vinyl stearate) this crystal form persists down to low temperatures.[9,31] It would seem reasonable, therefore, that enthalpic data from the literature for the fusion of the hexagonal modification of the *n*-alkanes (the $\alpha_H \rightarrow 1$ transition[25]) could represent the crystalline portion of the side chains in these homopolymers. Accordingly, heats of fusion for this transition at various chain lengths,[25] in the range of interest in this paper (n = 9–19), were fitted, with high statistical significance, by a first degree polynomial, in accordance with

$$\Delta H_f(\text{cal/mole}) = C + k(n) \tag{7}$$

where k is ΔH_f cal/mole-CH_2[32] and C is the contribution of the chain ends. The value of k, listed in Table III, clearly shows that the heat of fusion for the hexagonal form is much less than that found for the orthorhombic-to-liquid transition ($\beta_0 \rightarrow 1$)[25] found for the higher n-alkanes through polyethylene. Here k was considered to be 950 cal/mole-CH_2.[24] On substituting ΔH_f from eq. (7) for ΔH_{f0} in eq. (6), the crystallinity fraction is

$$x_c = [\Delta H_f(n)\ 14.026]/[C + k(n)] \tag{8}$$

where ΔH_f is in cal/g, the numerical constant is the molecular weight of a single methylene group, and n is the number of side-chain methylene groups, including the terminal methyl group. C was taken as zero here because the data of interest are the short-range enthalpic changes associated with the fusion of each methylene group.[33] Crystallinity, present in the side-chain only, x_{cs}, is

$$x_{cs} = f x_c \tag{9}$$

with f defined as

$$f = \mathrm{MW_{unit}}/(\mathrm{MW_{side-chain}} - 1.008) = \Delta H_f(\mathrm{cal/mole\text{-}unit})/\Delta H_f(\mathrm{cal/g})(n)14.026 \tag{10}$$

The number of crystalline CH_2 groups, including terminal methyl, in the side chain n_c is

$$n_c = x_{cs}(n) = (x_c \mathrm{MW_{unit}})/14.026 \tag{11}$$

and the number of amorphous methylene groups remaining n_a is

$$n_a = n - n_c \tag{12}$$

The quantities are listed in Table II.

Another approach to estimating crystallinity from these data considers the similarity in magnitude of k [eq. (7)] and α [eq. (2)] (see Table III) for the homopolymers. In eq. (2), the value of n at $\Delta H_{f0} = 0$ is given as

$$n_a' = \Delta H_{fe}/\alpha \tag{13}$$

where n_a' can be defined as the critical side-chain length below which crystallinity is absent. Assuming this value to be constant as side chain length increases without limit, then crystallinity becomes

$$x_c' = [(n - n_a')14.026]/MW_{unit} \tag{14}$$

Again the numbers of crystalline methylene groups is

$$n_c' = n - n_a' \tag{15}$$

If the assumptions inherent in eq. (8) and eq. (14) are correct, then the two methods should yield the same value for the crystallinity fraction. Thus

$$x_c = x_c' \tag{16}$$

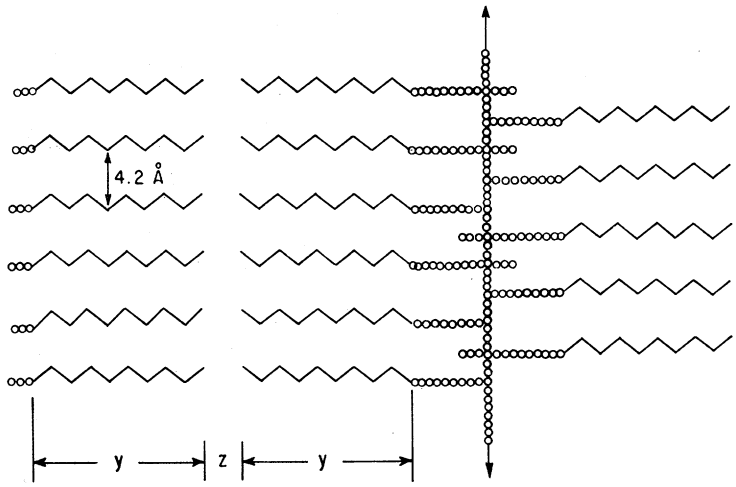

Fig. 4. Diagramatic representation of a proposed structure for poly(vinyl stearate) corresponding to a calculated long spacing of 24.64 Å for $n_c = 8.4$, in comparison to the found[28] long spacing of 27.00 Å.

The appropriate values listed in Table II confirm eq. (16). It is of special interest that the crystallinities obtained by using eqs. (8) and (14) received strong support from values reported by Greenberg and Alfrey[3] for the poly(n-alkyl acrylates) and poly(n-alkyl methacrylates), based on specific volumes; specific volumes should be sensitive to the crystalline order present in each chain unit.

A schematic diagram, illustrating the main features postulated for these homopolymers, is shown in Figure 4. Amorphous main-chain units are connected to 9 to 12 amorphous methylene groups which branch atactically from the main chain (small circles). These connect the ordered alkane chains, arranged in a hexagonal subcell, separated by 4.2 Å, as observed.[3,9,10,28,31] The ordered regions are packed end-to-end as shown and are stacked layer-on-layer to give three-dimensional order. Within the large error in estimating, the illustrated arrangement accounts for the long spacing of 27.0 Å found by Morosoff et al.[31] for poly(vinyl stearate). To calculate this spacing, the values of y and z employed by Jones[10] were used. The failure to observe in poly(vinyl stearate)[31] the low-angle reflections characteristic of the packing of the main chain units in crystalline polyoctadecene-1[10] provides additional confirmation for this structure. Significantly, in quenched polyoctadecene-1, these spacings are missing.[10]

A treatment of the entropy of fusion data in Table II remains. The parameters are listed in Table III. Of special interest are the values of ΔH_f per bond given in the last column of Table II. These were computed by using the ratio, $\Delta S_f/n_c$. The values are only slightly higher than the value of a polyethylene, 2.34 cal/mole-deg-bond.[17c] Quantitative comparisons are probably not warranted because of the differences in obtaining the bond entropy for the two types of homopolymers. It seems reasonable to

conclude that the relatively low values for the homopolymers having long side chains are a manifestation of the high solid-state entropy conferred by the hexagonal packing present in the crystallites.[25] Using eq. (17) to calculate the entropy per bond for the hexagonal crystal form of n-alkanes yields $[(C + kn)/T_m]/n$, where T_m is the melting temperature[25] and C and k are from Table II; this gave an exceptionally low average value of 1.9 cal/mole-deg for the transition.

SUMMARY AND CONCLUSIONS

From the thermodynamic data involving heats and entropies of fusion and melting transitions, for three structurally varied series of homologs having long side chains, it was concluded that only the outer paraffinic methylenes were present in the crystal lattice. Specific information leading to this conclusion were: (a) scanning curves reflecting the distribution of crystallite sizes become narrower as the side chain becomes longer; (b) solvolysis of the main chain by methanol allowed the entrance of more methylene units into the lattice, thereby raising the melting point above that of the bulk state; (c) phase diagrams of mixtures of structurally different monomers and homopolymers, as well as for selected copolymers, showed only isomorphism in the polymeric examples; (d) crystallinity estimates obtained for each structural unit, assuming that only hexagonal paraffinic chains were in the crystal, were in agreement with proposed unit-cell models derived from the literature based on x-ray diffraction measurements.

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